

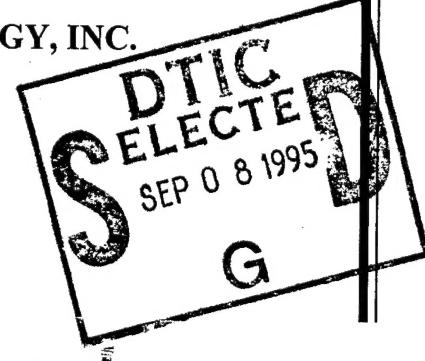
AL/OE-TR-1994-0075



**OVERVIEW OF THE VAPOR GENERATION AND
ANALYSIS PARAMETERS OF THE PETROLEUM - AND SHALE -
DERIVED FUEL STUDIES CONDUCTED IN THOMAS DOME EXPOSURE
CHAMBERS AT THE TOXIC HAZARDS RESEARCH UNIT
WRIGHT-PATTERSON AFB (DAYTON), OHIO 1973-1983**

H. F. Leahy

MANTECH ENVIRONMENTAL TECHNOLOGY, INC.
P.O. BOX 31009
DAYTON, OH 45437



May 1994

19950906 071

FINAL REPORT FOR THE PERIOD JANUARY 1973 TO DECEMBER 1983

Approved for public release; distribution is unlimited

**AIR FORCE MATERIEL COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433-7901**

NOTICES

When US Government drawings, specifications or other data are used for any purpose other than a definitely related Government procurement operation, the Government thereby incurs no responsibility nor any obligation whatsoever, and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data is not to be regarded by implication or otherwise, as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

Please do not request copies of this report from the Armstrong Laboratory. Additional copies may be purchased from:

National Technical Information Service
5285 Port Royal Road
Springfield, Virginia 22161

Federal Government agencies and their contractors registered with the Defense Technical Information Center should direct requests for copies of this report to:

Defense Technical Information Center
Cameron Station
Alexandria, Virginia 22314

DISCLAIMER

This Technical Report is published as received and has not been edited by the Technical Editing Staff of the Armstrong Laboratory.

TECHNICAL REVIEW AND APPROVAL

AL/0E-TR-1994-0075

The experiments reported herein were conducted according to the "Guide for the Care and Use of Laboratory Animals," Institute of Laboratory Animal Resources, National Research Council.

This report has been reviewed by the Office of Public Affairs (PA) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.

FOR THE COMMANDER

Terry A. Childress
TERRY A. CHILDRESS, Lt Col, USAF, BSC
Director, Toxicology Division
Armstrong Laboratory

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information including suggestions for reducing this burden to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188
<p>1. AGENCY USE ONLY (Leave Blank)</p>			
<p>2. REPORT DATE May 1994</p>		<p>3. REPORT TYPE AND DATES COVERED Final - January 1973 - December 1983</p>	
<p>4. TITLE AND SUBTITLE Overview of the Vapor Generation and Analysis Parameters of the Petroleum- and Shale-Derived Fuel Studies Conducted in Thomas Dome Exposure Chambers at the Toxic Hazards Research Unit, Wright-Patterson AFB (Dayton), Ohio, 1973-1983</p>		<p>5. FUNDING NUMBERS Contract F33615-90-C-0532 PE 62202F PR 6302 TA 630200 WU 63020002</p>	
<p>6. AUTHOR(S) H.F. Leahy</p>		<p>8. PERFORMING ORGANIZATION REPORT NUMBER 4300-9405</p>	
<p>7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) ManTech Environmental Technology, Inc. Toxic Hazards Research Unit P.O. Box 31009 Dayton, OH 45437-0009</p>		<p>10. SPONSORING;MONITORING AGENCY REPORT NUMBER AL/OE-TR-1994-0075</p>	
<p>9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Armstrong Laboratory, Occupational and Environmental Health Directorate Toxicology Division, Human Systems Center Air Force Materiel Command Wright-Patterson AFB OH 45433-7400</p>			
<p>11. SUPPLEMENTARY NOTES</p>			
<p>12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.</p>		<p>12b. DISTRIBUTION CODE</p>	
<p>13. ABSTRACT (Maximum 200 words)</p> <p>Over a decade ago (1973-1983), a series of long-term inhalation exposures were performed to study the toxicity of a number of aviation and marine fuels derived from petroleum and compare results with those derived from shale. These included JP-4, JP-5, and diesel fuel marine, as well as some specialty petroleum-derived fuels JP-7, JP-8, and JP-TS. The Thomas Domes located in the Armstrong Laboratory at Wright-Patterson Air Force Base (Dayton), Ohio, were ideally suited for these studies because of both the large capacity for inhalation exposure of the mixed animal complement and the convenience of entry without interrupting continuous exposures. The target total hydrocarbon (TH) concentrations ranged from 0.05 to 5.0 mg/L. The concentration levels of TH vapors were limited by the effective vapor pressure of the type of fuel and, if exceeded, the formation of condensate aerosols in the exposure chamber. The TH vapor generation and analytical equipment is described. Advances in gas chromatographic technology during the period covered provided a variety of qualitative pictures of the fuel, vapor, and waste TH components. Hydrocarbons above C14 existed only in very low concentrations in any of the vapors.</p>			
<p>14. SUBJECT TERMS Inhalation Studies Shale-Derived Fuel</p>		<p>15. NUMBER OF PAGES 31</p>	
<p>Petroleum-Derived Fuel Thomas Dome</p>		<p>16. PRICE CODE</p>	
<p>17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED</p>	<p>18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED</p>	<p>19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED</p>	<p>20. LIMITATION OF ABSTRACT UL</p>

THIS PAGE INTENTIONALLY LEFT BLANK

PREFACE

This report will describe some of the petroleum and shale fuels tested, the basic methods involved in the generation and analysis of chamber atmospheres, as well as some of the problems encountered during the studies performed in Thomas dome inhalation chambers. The work was performed at the Toxic Hazards Research Unit, located at Wright-Patterson Air Force Base, Ohio. This document serves as a final report on work conducted from 1973 to 1983 under U.S. Air Force Contract Nos. F33615-73-C-4059, F33615-76-C-5005, and F33615-80-C-0512. Contract Technical Monitors during this time period were K.C. Back and M.K. Pinkerton.

This report was prepared at the Toxic Hazards Research Unit, ManTech Environmental Technology, Inc., under Department of the Air Force Contract No. F33615-90-C-0532, Study No. F28; Contract Technical Monitor for the U.S. Air Force, Armstrong Laboratory, Toxicology Division, was Lt Col Terry A. Childress.

Accesion For	
NTIS CRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification _____	
By _____	
Distribution / _____	
Availability Codes	
Dist	Avail and / or Special
A-1	

TABLE OF CONTENTS

SECTION	PAGE
PREFACE	1
LIST OF FIGURES	3
LIST OF TABLES	4
ABBREVIATIONS	5
1 INTRODUCTION	6
2 ANALYSIS	7
Mass Composition	7
Component Composition	7
Chromatography Equipment	15
Aerosol	17
Target Concentrations	17
3 GENERATION	18
Evaporation Tower System	18
Evaporation Tower Operation	19
4 RESULTS	21
Vapor	21
Fuel Description	22
Operational Problems	24
1. Temperature	24
2. Splashing	24
3. Sampling	25
4. Chromatography	25
Operational Parameters	26
5 REFERENCES	29

LIST OF FIGURES

FIGURE	PAGE
1 Chromatograms of shale-derived JP-4 fuel: (a) liquid fuel, (b) chamber vapor, (c) evaporation tower waste	8
2 Chromatograms of JP-5 fuel: (a) shale-derived fuel, (b) petroleum-derived fuel	9
3 Chromatogram of chamber vapor of shale JP-5 containing significant aviation gas	9
4 Chromatograms of shale-derived JP-5 fuel: (a) liquid fuel, (b) chamber vapor, (c) evaporation tower waste	10
5 Chromatograms of shale-derived DFM fuel: (a) liquid fuel, (b) chamber vapor, (c) evaporation tower waste	11
6 Chromatograms of JP-7: (a) chamber vapor, (b) liquid fuel	12
7 Chromatograms of JP-TS: (a) chamber vapor, (b) liquid fuel	13
8 Chromatograms of JP-8: (a) chamber vapor, (b) liquid fuel	14
9 Bar graph plot of area slices data for shale JP-4 comparing relative percent of total peak area for vapor, liquid, and waste samples	16
10 Bar graph plot of area slices data for shale DFM comparing relative percent of total peak area for vapor and liquid sample	16
11 Probability plot of area slice data to determine the 16, 50, and 84% temperature cut-off points	23

LIST OF TABLES

TABLE	PAGE
1 Gas Chromatographic Area Slice Integration Analysis — Comparison of the Liquid Shale DFM with the Chamber Vapor	22
2 Simplified Fuel Description Using Data of Accumulated Percent Peak Area from Simulated Distillation of Shale JP-4	24
3 An Estimation of the Distribution of the Major Alkane Fractions Present in the Three Phases of the Fuels	26
4 Fuel Study Generation Conditions for Petroleum- and Shale-Derived JP-4	27
5 Fuel Study Generation Conditions for Petroleum- and Shale-Derived JP-5 and DFM	27
6 Fuel Study Generation Conditions for JP-7, JP-TS, and JP-8	28

ABBREVIATIONS

AvGas	Aviation gasoline
DFM	Diesel fuel marine
FID	Flame ionization detector
ft	Foot
gal	Gallon
in.	Inch
L	Liter
mg	Milligram
min	Minute
O.D.	Outer diameter
ppm	Parts per million
psi	Pounds per square inch
SDFM	Shale-derived diesel fuel marine
TH	Total hydrocarbon
TPH	Total petroleum hydrocarbon
V	Volt
Ω	Ohm

SECTION 1

INTRODUCTION

Inhalation toxicology of fuels, solvents, and hydraulic fluids has been an important part of the work at the Toxic Hazards Research Unit over the past 20 or more years. During this time, there were many changes in the equipment available to describe the exposures, while at the same time, equipment to produce them was only slightly modified. This report will be limited to some of the petroleum and shale fuels tested and will describe the basic methods involved in generation and analysis of the chamber atmospheres and problems encountered in the process. These studies were performed in the Thomas Dome inhalation chambers (Thomas, 1965), which are located in the Armstrong Laboratory at Wright-Patterson Air Force Base (Dayton), Ohio. The Thomas domes are unique exposure chambers adaptable to both altitude and ambient continuous studies of both aerosols and vapors.

SECTION 2

ANALYSIS

Mass Composition

All petroleum-and shale-derived fuels are complex mixtures of mainly aliphatic and some aromatic compounds, while the most distinguishing feature is the relative composition of these compounds based on the distillation cut temperatures. The specific mixture not only is influenced by end use, which determines the physical characteristics such as volatility and viscosity, but also the chemical composition is a function of the source of the crude and the cracking process. Each of the fuels used in these studies is from a single batch of a fuel passing the physical requirements for that fuel type.

Quantifying the total petroleum (or shale) hydrocarbon (TPH) of such a complex mixture is possible with use of a flame ionization detector (FID) adapted for continuous analysis. The FID response to the mixed alkyls is based essentially on the mass concentration of the vapor, independent of the chain length. This fact permitted calibration using known mass concentrations of a convenient hydrocarbon. Beckman 400 hydrocarbon analyzers (Beckman Inst. Co., Fullerton, CA) were used for all TPH analyses. Propane, hexane, and heptane, as well as benzene, have been used as quantifying standards. Hexane has been recommended as a universal standard for TPH calibration.

Initially, the number of hydrocarbon analyzers was limited, and sample dilution was necessary for analysis of two chambers of different concentrations with a single analyzer. Attention to the dilution was essential for accuracy. Later, each chamber, as well as an industrial hygiene system, was equipped with an analyzer.

Component Composition

During the initial studies, gas chromatography was used to determine the benzene concentration of the fuel and the chamber atmosphere. Samples from each of the supply drums were chromatographed and areas of a number of the peaks eluting during the first 20 min were used to compare the supply drums of fuel for quality control.

The use of packed columns, the lack of column oven temperature programming, and no automatic integration limited data acquisition for the first studies. But with the availability in time of increased analytical capability, more information was made available. These data were not always part of the study request but were an attempt to expand analytical capability and to supply quality control information. The study protocols called for a mass concentration without a definitive cut description, while the authors

of the protocols assumed the exposure would resemble that following a fuel spill. A representative set of the available chromatograms is included as a supplement with this report (Figures 1 to 8).

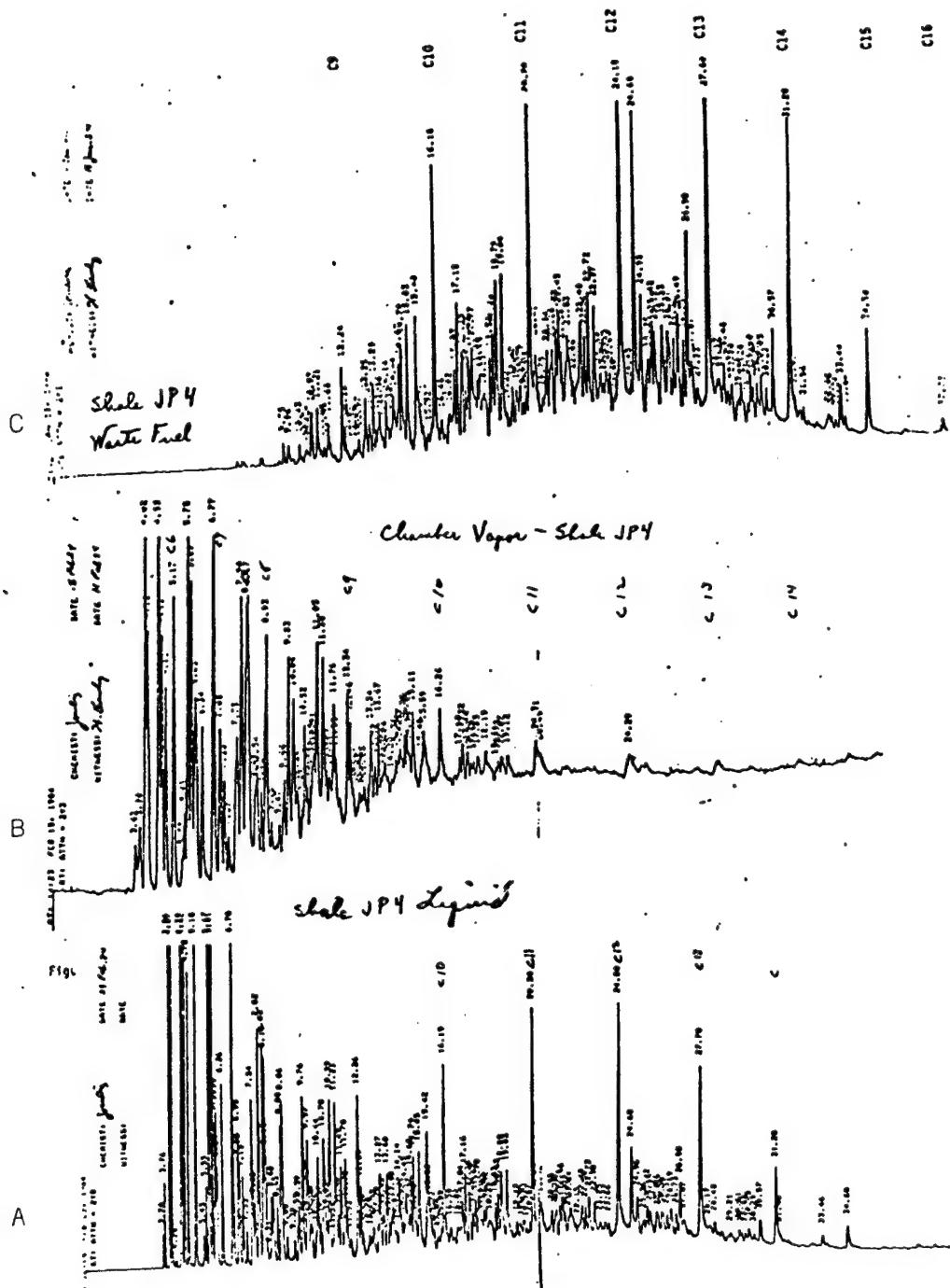


Figure 1. Chromatograms of shale-derived JP-4 fuel: (a) liquid fuel, (b) chamber vapor, (c) evaporation tower waste.

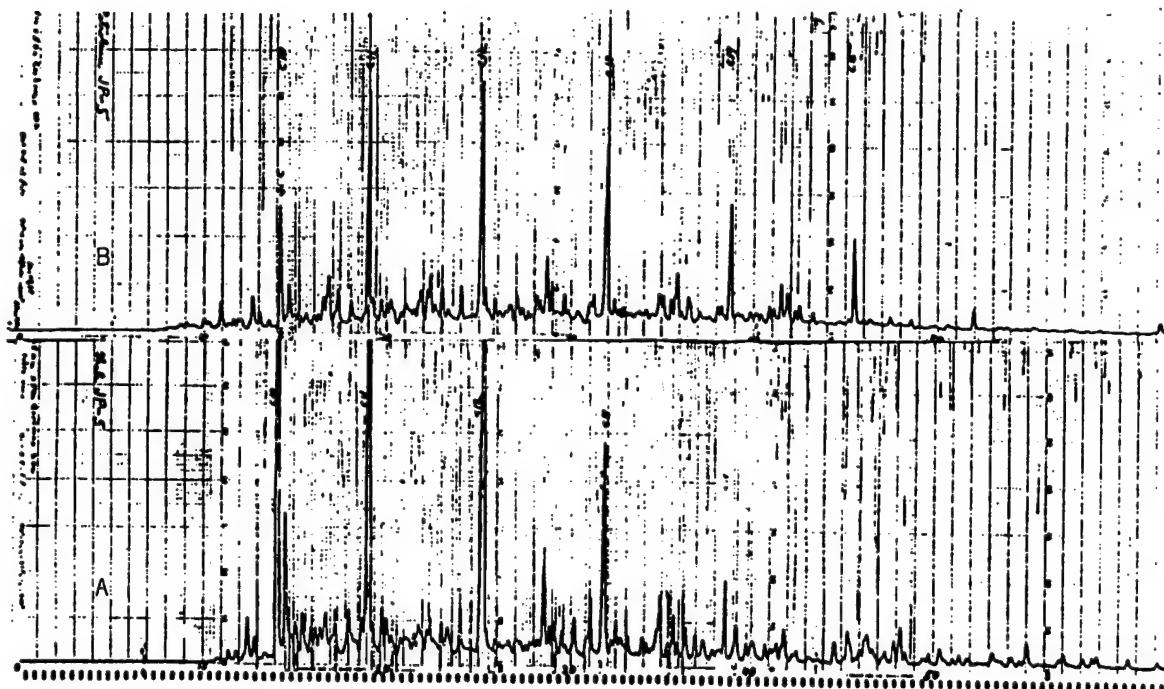


Figure 2. Chromatograms of JP-5 fuel: (a) shale-derived fuel, (b) petroleum-derived fuel.

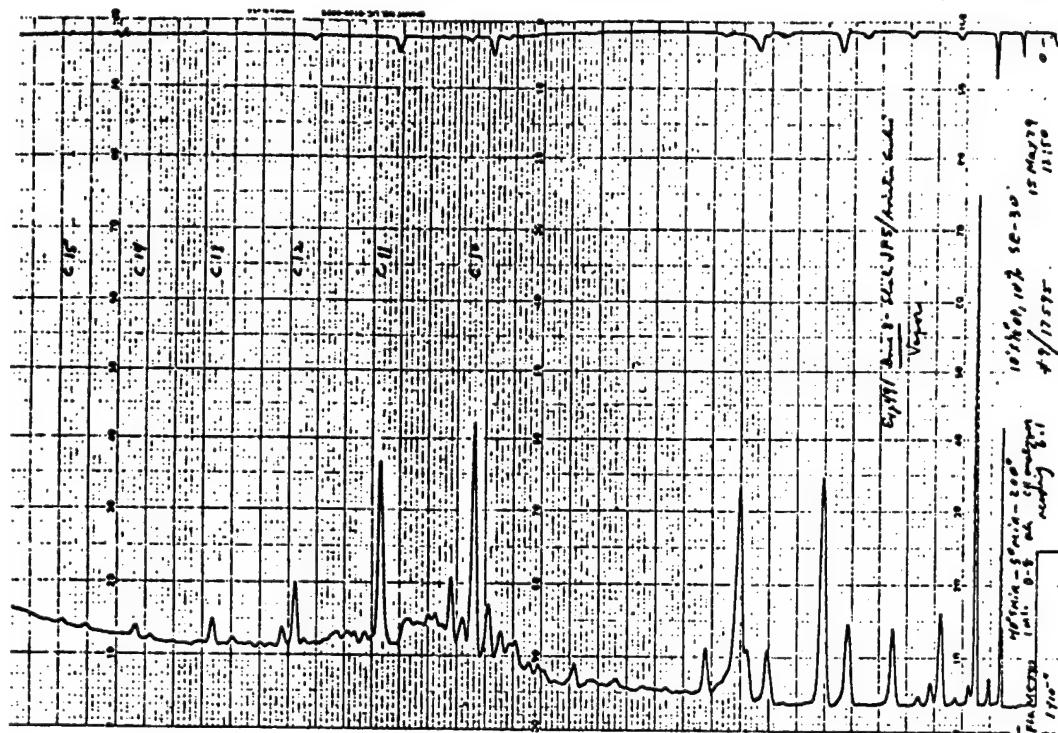


Figure 3. Chromatogram of chamber vapor of shale JP-5 containing significant aviation gas.

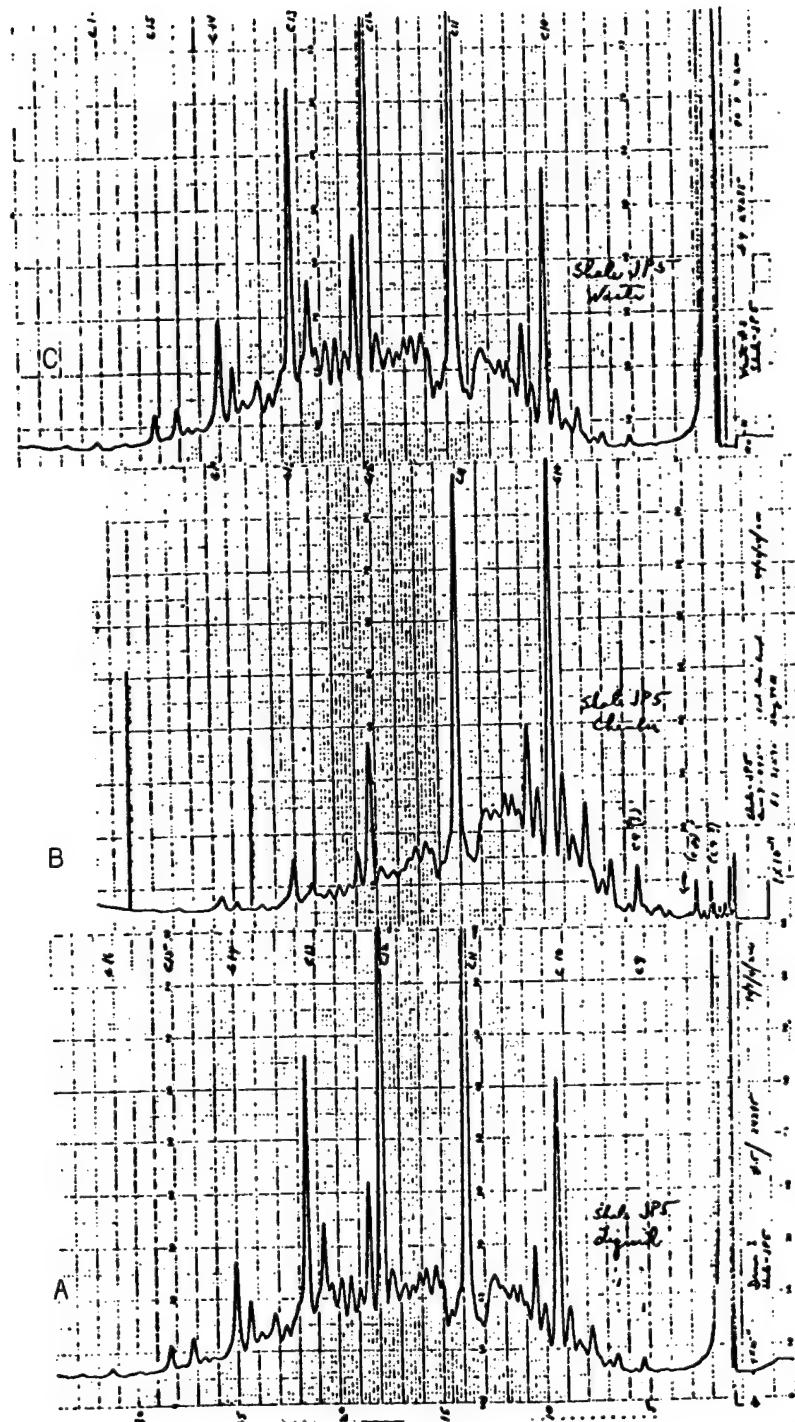


Figure 4. Chromatograms of shale-derived JP-5 fuel: (a) liquid fuel, (b) chamber vapor, (c) evaporation tower waste.

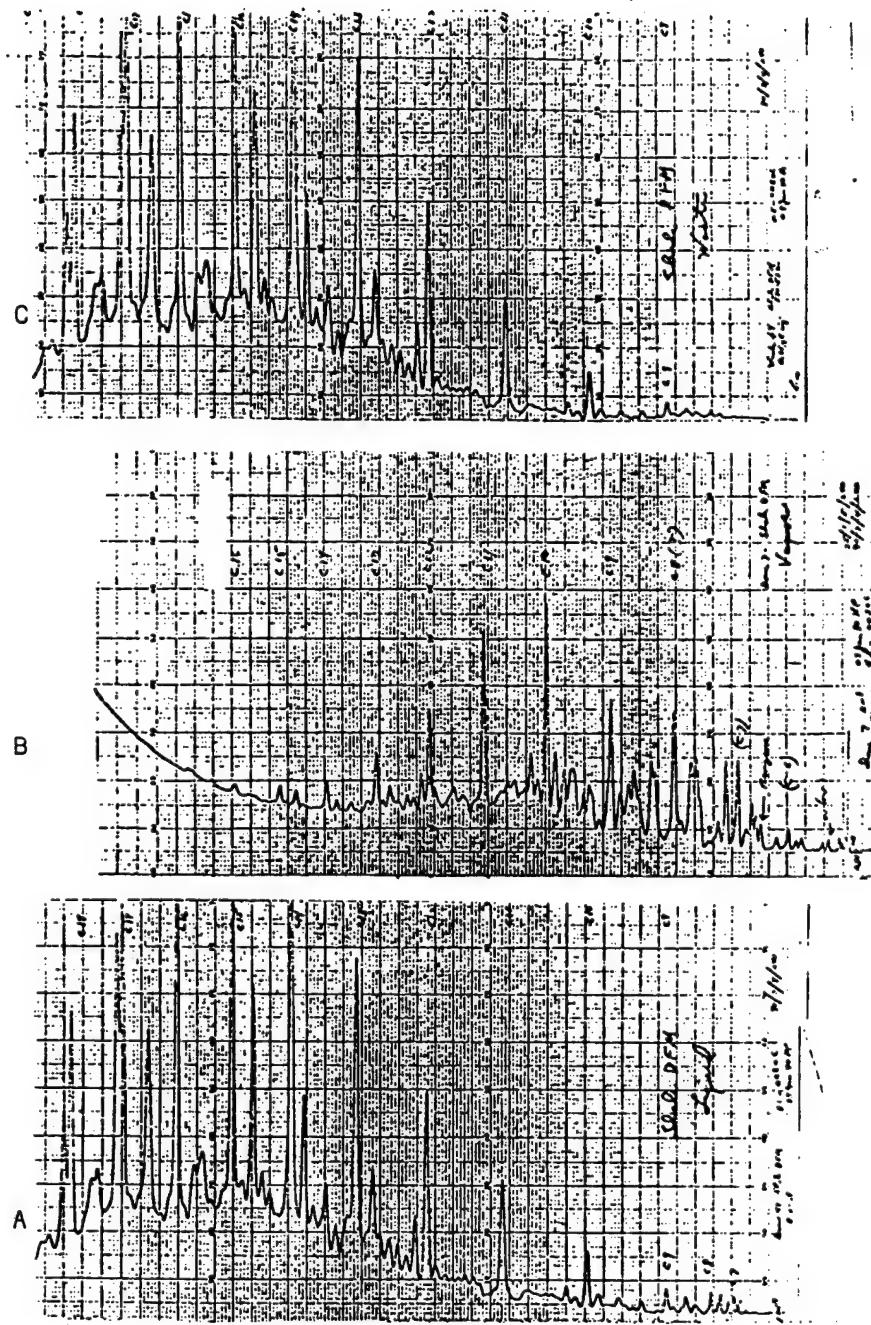


Figure 5. Chromatograms of shale-derived DFM fuel: (a) liquid fuel, (b) chamber vapor, (c) evaporation tower waste.

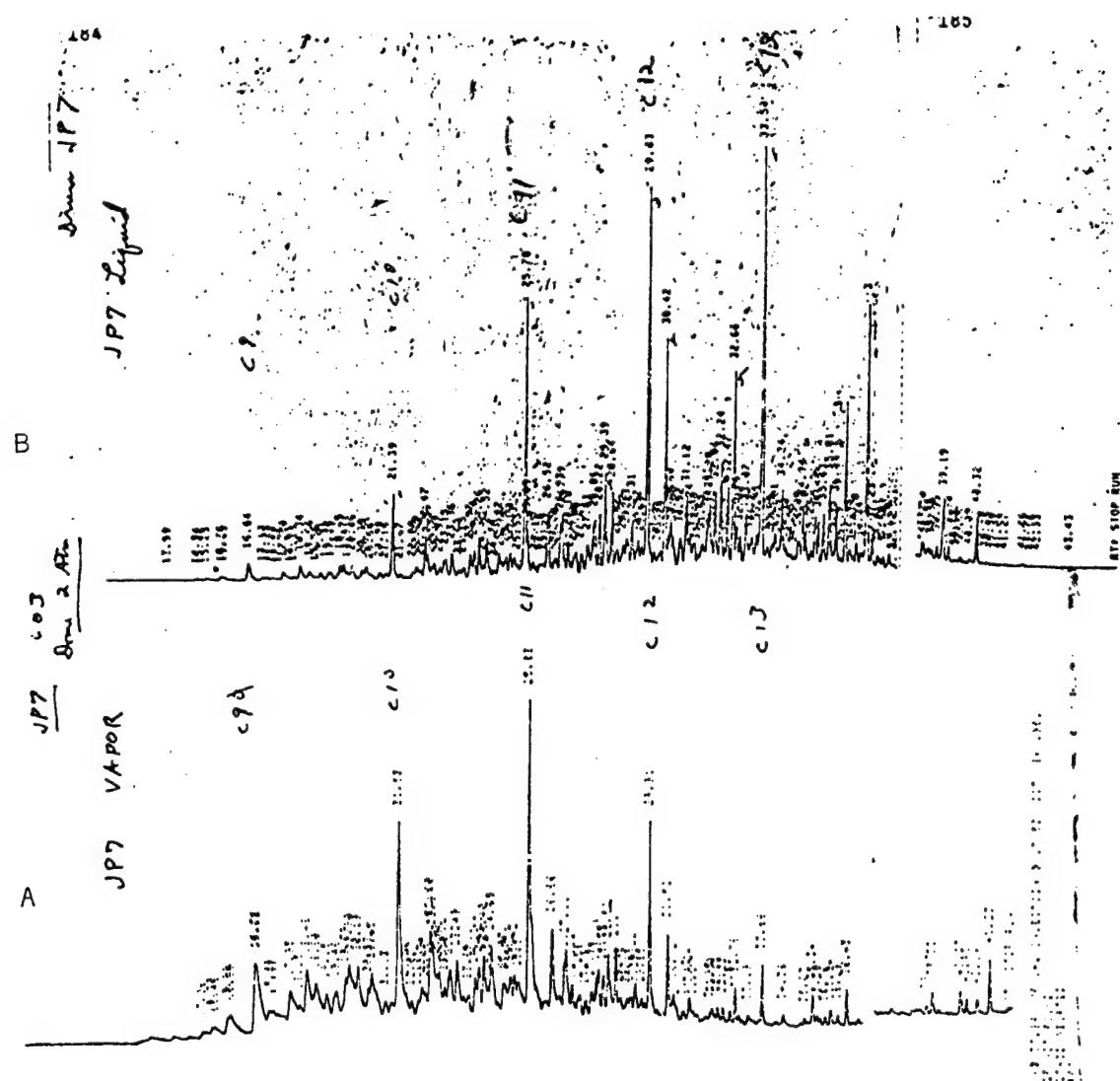


Figure 6. Chromatograms of JP-7: (a) chamber vapor, (b) liquid fuel.

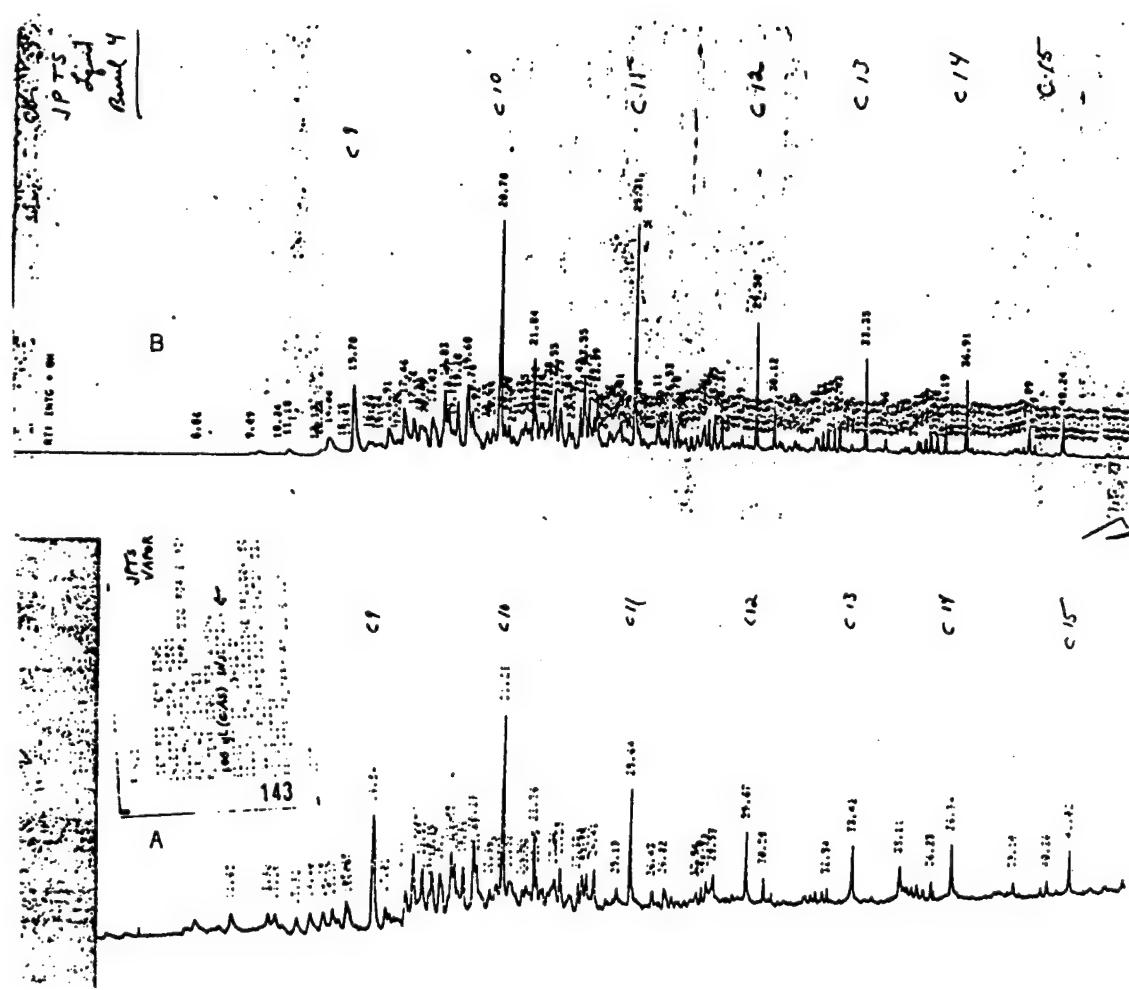


Figure 7. Chromatograms of JP-TS: (a) chamber vapor, (b) liquid fuel.

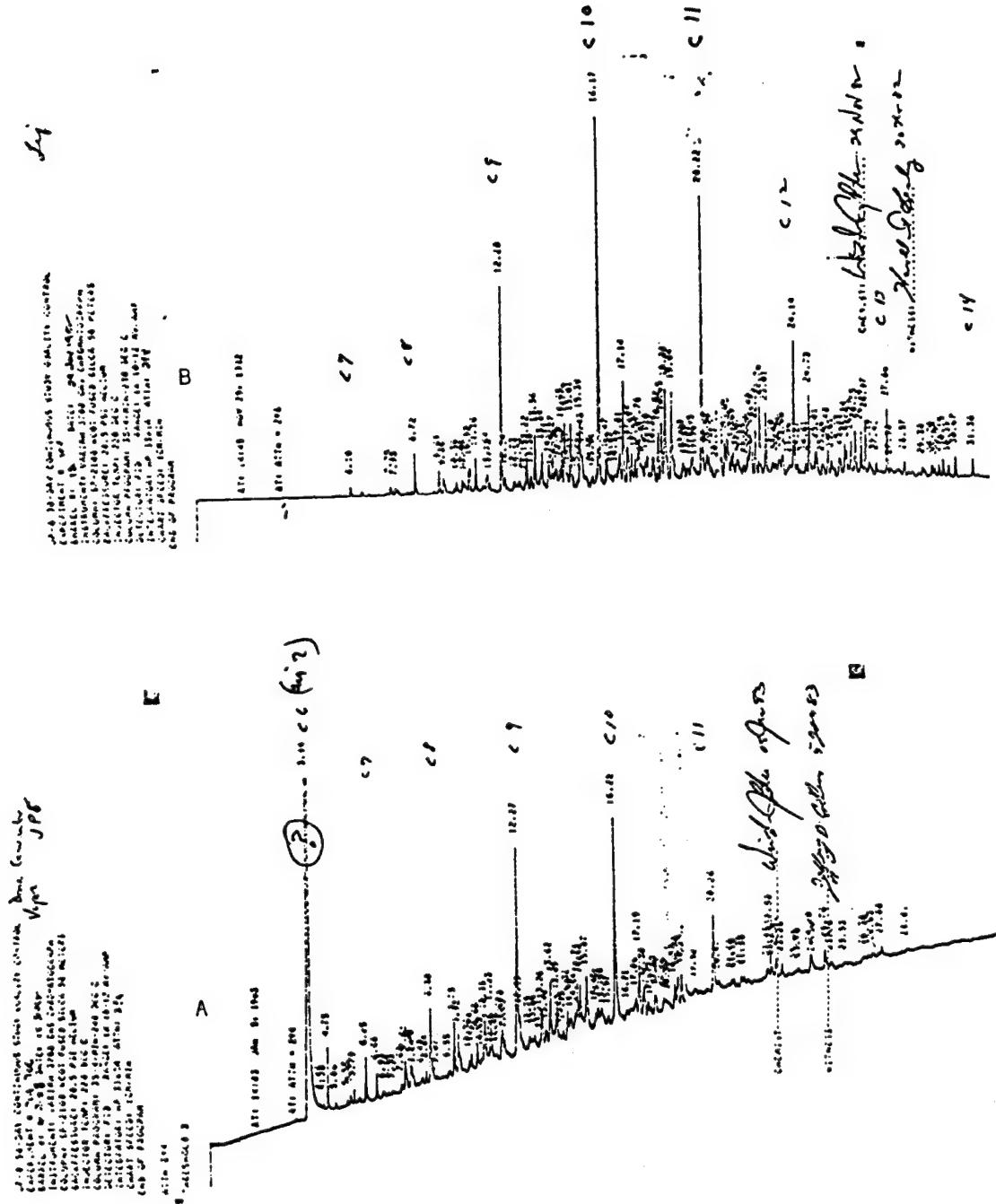


Figure 8. Chromatograms of JP-8: (a) chamber vapor, (b) liquid fuel.

Chromatography Equipment

A Varian 1200 (Varian Inst. Corp., Walnut Creek, CA) with packed columns supplied the information for benzene analysis in studies conducted prior to 1978. Chromatograms were limited to the first 20 min of an isothermal run; a System One computing integrator (Spectra Physics, Santa Clara, CA) was used for some quality control data.

When the Varian 3700 chromatograph (Varian Inst. Corp., Walnut Creek, CA) was obtained and the first temperature programmed chromatograms were developed, the complexity of fuels was first appreciated and the problems of integration were encountered. The System One memory was insufficient for the number of peaks obtained when capillary columns were introduced.

A constant problem for any fuel's chromatography is the overwhelming number of peaks of very similar materials, which results in a rising baseline from both overlapping peaks and temperature programming. Accurate integration of these factors becomes a difficult problem, if not an impossibility. Although hard numbers from very similar integrations are not available from all of the different studies represented here, visualization of some representative chromatograms is of value for comprehension of the fact that the exposures were more alike qualitatively than one might have expected (Figures 1, 4, 5, 6, 7, and 8).

The acquisition of an HP-5780 computing integrator in 1978 allowed better data analysis with improved integration and the ability to reintegrate and run area slices programs (Figures 9 and 10). These demonstrate the significant differences of liquid, vapor, and waste.

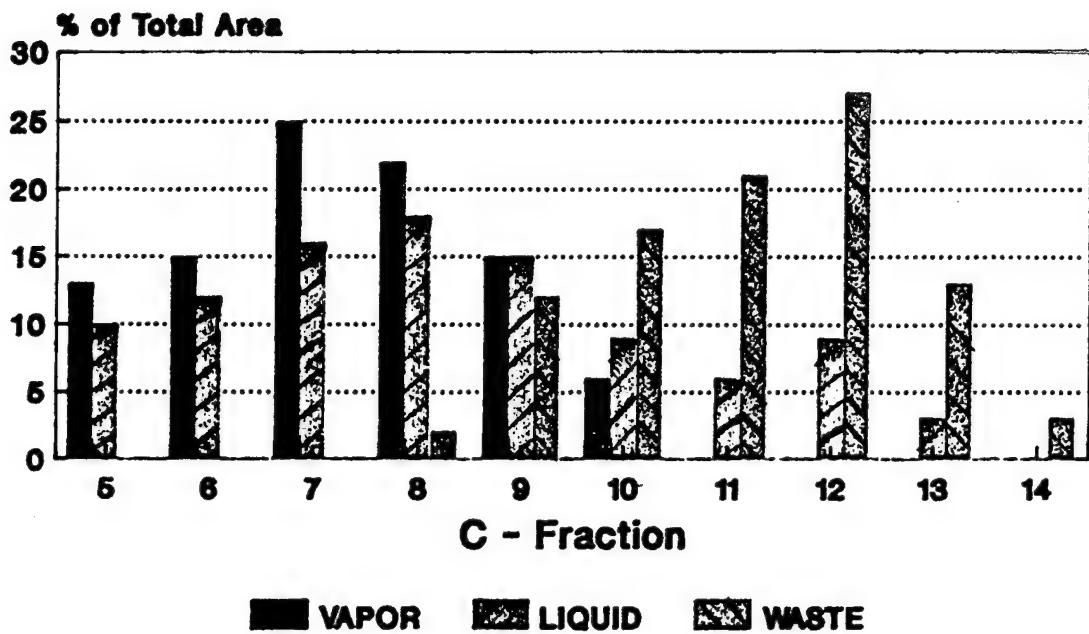


Figure 9. Bar graph plot of area slices data for shale JP-4 comparing relative percent of total peak area for vapor, liquid, and waste samples.

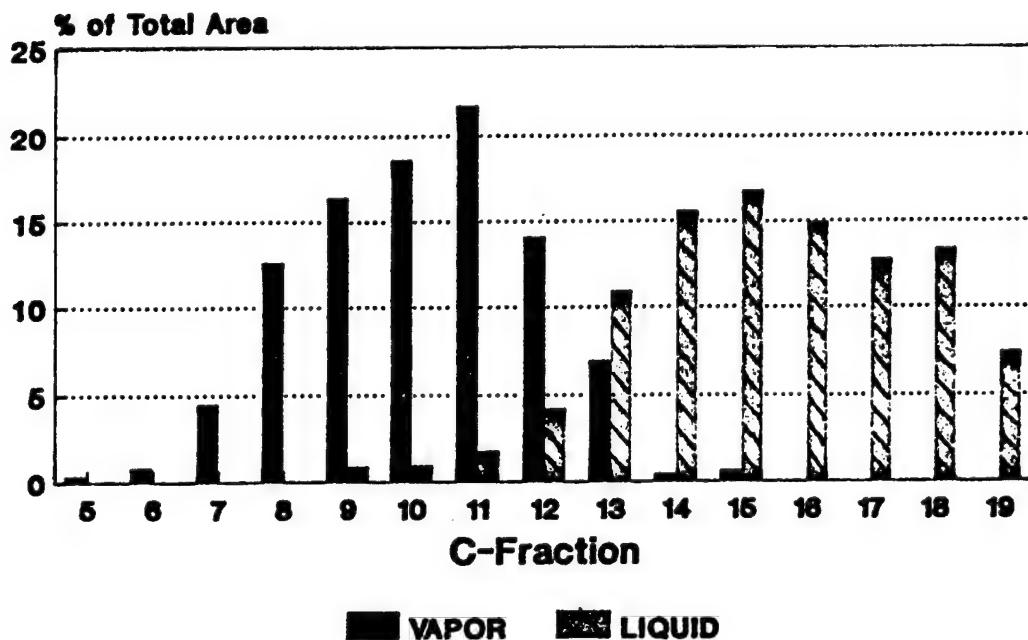


Figure 10. Bar graph plot of area slices data for shale DFM comparing relative percent of total peak area for vapor and liquid sample.

Aerosol

Shortly after the start of the Petroleum JP-5 study (1977), a condensate aerosol caused the loss of many of the mice, necessitating a restart of the study with replacements and at a lower concentration. Cold chamber temperatures, a high vaporization temperature, and low chamber air flow contributed to the problem. Generation conditions were thereafter tested with respect to the potential for an aerosol episode before the start of each new exposure, and target concentrations were scaled downwards if a problem was encountered. Also, routine aerosol counting was introduced using a Model 225 aerosol particle counter (Royco Instruments, Inc., Menlo Park, CA) for the remainder of the fuel studies.

Formation of the condensate aerosol appeared to be a critical event triggered by evaporator temperature that was too high, or chamber temperature that was too low. The only effective way to increase the TPH for the heavier fuels was some combination of an increase of fuel flow and evaporator air supply, thereby supplying more of the lighter chain components for vaporization.

For valid sampling with the Royco particle counter, attention had to be paid to the dome/dome room differential pressure due to the type of sample pump in the instrument.

Target Concentrations

The first study (348-351, 1973) of petroleum-based JP-4 targeted a specific benzene concentration in the atmosphere as well as the total hydrocarbon present. At that time, the benzene concentration of fuels was significantly higher than any fuels used during subsequent studies. With the 5 and 2.5 mg/L TPH vapor exposures, a 25 and 12.5 ppm exposure to benzene was accomplished. High fuel flow rates (30 to 40 mL/min) and low generator temperatures were combined in this study to favor an increase of benzene in the vapor.

The next study request, that for petroleum JP-5 (416-418, 1977), targeted a 1.5 mg/L TPH concentration with 10 ppm benzene. The fuel not only contained insufficient benzene to attain 10 ppm, but the total quantity of fuel available was limited. Only enough supply was available for use of 10 mL/min/tower for the length of the exposure. The attempt to operate at 1.5 mg/L with the limited flow and a generation temperature about 135 °F ended with an aerosol excursion. The study was restarted with fresh animals at a lower target concentration of 0.75 mg/L.

After experiencing the aerosol problem, the requested TPH concentrations for all further studies were tested and modified when found necessary. The fuel evaporating temperature was kept below 135 °F and fuel flow rate, as well as evaporator air flow, were increased to raise TPH vapor output. If all else failed, the target concentration was lowered to prevent formation of aerosol.

SECTION 3

GENERATION

Evaporation Tower System

The evaporation towers used were common for all of the fuel studies as well as for a number of solvent and specialty fuel studies where an output of a high volume of vapor was required.

The central zone of the glass tower was a cylinder 13 in. long by 1-3/4 in. O.D. It had a 13-turn spiral, 9 in. long, impressed in the wall to hold a heating coil and lengthen the vaporization path. The top reduced to a "T" with a 1-in. O.D. right arm for vapor exhaust and a 1/4-in. connector for input fuel. The bottom reduced to a 1-in. O.D. glass tubing connected to a double "T" of stainless steel tubing. Pipe fittings at this connection served for waste fuel drain and carrier air input.

Up to three towers were used to generate the total amount of fuel vapor required. To ensure qualitatively comparable exposures in the chambers, the tower outputs were combined in a manifold and routed to the domes by controlled volume flow proportional to the specified dome concentration. Fine chamber concentration control was accomplished during normal operation by minor changes of the individual dome flows.

Some of the heat energy for vaporization was supplied with the incoming air, but most came from an electrically heated coil wrapped around the tower. This was composed of a 1/4-in. close coiled nicrome wire (B.& S. 20-gauge, 1.1 Ω /in., Wooge Manufacturing Co., Chicago, IL) approximately 6 ft long. The temperature of the tower output (air and vapor mix) was monitored using probes in the fittings at the top. There was no measure of the internal tower wall temperature. The waste fuel temperature also was monitored.

During the initial studies, the desired output temperature was obtained using 120 V AC power rheostats, which supplied a constant voltage to the coil. The efficiency of the vapor output was affected by the temperature of the incoming air as well as that of the vaporization surface area. The input power was manually modified in response to the output temperature. The later studies made use of a proportional temperature controller that continuously monitored the tower output temperature and modified the input power to maintain a set temperature automatically. This eliminated the decreased output from cold temperatures, and actually replaced it with a slight increase of vapor output during cold external conditions.

The input fuel flow rate was controlled with a needle valve and monitored using Fisher & Porter rotameters (Warminster, PA). Fuel was supplied to the system directly from a 45 gal drum pressurized

at 5 to 8 psi. The control valve was positioned after the rotameter to prevent effervescence in the flow tube. The waste fuel flow was partially throttled to reduce the loss of tower vapor output and was pumped from an intermediate catch tank to a waste collecting drum. Redundant supply and waste systems allowed continuous operation while replacing drums.

The generation system was protected from fire by monitoring probes and a solenoid switch set to shut off the fuel flow in case of temperature overrun of either the fuel vapors or the waste fuel.

Evaporation Tower Operation

Except for the first two studies where a specific benzene concentration also was expected, the goal was to supply a specific and constant TPH concentration without creating an aerosol. The conditions required to attain the target concentrations were, in general, established empirically.

The evaporator towers operated as counter flow systems. The fuel entered the top of the towers in a 1/8-in. O.D. teflon tube and the air entered at the bottom, bypassing the spent fuel. The fuel flowed from a point above the heating coil where the tube touched the glass, then down the sidewall of the evaporator in an uncontrolled stream. As it descended, the composition of both the fuel and the vapors generated were in a dynamic state of change. The upper tower temperature sensor monitored the mixed air and fuel vapor leaving the tower, not that of the evaporating surface area of the tower, while the lower tower sensor monitored the temperature of the spent fuel. Consistent tower operation and pooling of the outputs of two or more towers provided qualitatively similar output for the operation of up to three chambers.

At a specific temperature, the effective vapor pressure of an individual component in a mixture is a function of its vapor pressure times its mole percent concentration multiplied by an activity coefficient of the system. The activity coefficient is related to the solvent, the temperature, and the pressure. For the mixed components of the paraffinic series, this latter effect should be a minor factor due to the similarity of the components (Bishop, 1981). The complexity of the evaporation of the fuel was not only due to the multiplicity of components, but also of its changing percent composition and temperature as it flowed down the tower wall. The composition of vapors obtained was a compromise somewhere between a headspace sample and the original fuel with a significant reduction after C13 due to the effectively low vapor pressures of the longer chain hydrocarbons.

In the system as operated, increasing the fuel flow rate, short of initiating splashing, while maintaining air flow rates resulted in a greater TPH output due to the presence of more volatile components available for stripping, as well as from the additional heat supplied to maintain the output temperature of the vapor

and air mix. This would favor a relative increase in the front end component of the vapor. An increase of the carrier air flow alone also increased the TPH output by removing more air per unit time while also causing more heat input to maintain the same output temperature. This would shift the vapor to contain somewhat more of the less volatile component.

On the other hand, from the same fuel and air flow, but at a higher operational temperature, the TPH vapor output also could readily be increased. But as the fuel temperature increases, the vapor pressures of the heavier hydrocarbons increase relatively faster than those of lighter ones, while on cooling, the reverse occurs, thus contributing to the probability of an oversaturated system, followed by formation of a condensate aerosol. An upper tower temperature of about 135 °F was empirically determined to be near a critical upper limit for operation of the system with acceptable aerosol measurement.

SECTION 4

RESULTS

Vapor

The overall effect due to (a) the nature of the fuels (broad distillation cuts), (b) the manner of achieving the target concentrations, and (c) the temperature restriction on vapor generation was to favor whatever lighter fraction was present. The target concentrations for JP-4 were easily met because of the predominance of the light hydrocarbon fraction. In an attempt to achieve the targeted concentration with increased heat due to a limitation of available fuel for the project, the first JP-5 study experienced a condensate aerosol on cooling of the vapors. That study was restarted at a lower target concentration. The most extreme example of the difference of vapor from the parent fuel was the chamber atmosphere produced from shale-derived diesel fuel marine (SDFM), where over 50% of the TPH vapors were from decane (C10) and lower molecular weight components, which had represented less than 2% of the original fuel (Table 1 and Figure 10). The volatility restrictions of heavier fuels were overcome by the increased flow rate of fuels through the towers and the lower targeted chamber TPH concentrations. Thus, the exposure atmospheres of both petroleum and diesel, JP-5 and DFM, also JP-7, JP-TS, and JP-8, were more similar qualitatively than would have been expected if considering only the starting fuel composition. A series of chromatograms, where available, compare qualitatively the chamber vapors with input fuels and spent fuels.

**TABLE 1. GAS CHROMATOGRAPHIC AREA SLICE INTEGRATION ANALYSIS -
COMPARISON OF THE LIQUID SHALE DFM WITH THE CHAMBER VAPOR**

Fraction	Liquid DFM		Chamber Atmosphere	
	% of Total Area	Cumulative %	% of Total Area	Cumulative %
< C5	N.I.	-	1.0	1.00
C5	N.I.	-	0.35	1.35
C6	N.I.	-	0.83	2.18
C7	N.I.	-	4.51	6.69
C8	N.I.	-	12.59	19.28
C9	0.90	0.90	16.41	35.69
C10	0.98	1.88	18.60	54.29
C11	1.81	3.69	21.71	76.00
C12	4.22	7.91	14.08	90.08
C13	10.90	18.81	6.93	97.01
C14	15.56	34.37	0.44	97.45
C15	16.77	51.15	0.63	98.08
C16	14.89	66.03	N.I.	-
C17	12.74	78.77	N.I.	-
C18	13.33	92.10	N.I.	-
C19	7.39	99.49	N.I.	-
C20	0.52	100.00	N.I.	-

Note: (a) The fractions (area slices) are designated by the normal alkane number and include all compounds between the previous normal alkane up to and including the designated normal alkane.

(b) N.I. = not integrated.

Fuel Description

With availability of good chromatography and integration, the composition of a complex fuel or fuel vapor can be described graphically or numerically in a simpler form by application of the concepts of simulated distillation and area slicing. This can be accomplished by dividing the chromatogram into logical subunits, in this case by the normal alkanes, and summing the peak areas within the subunits.

By plotting on probability graph paper the accumulated percent area of the slices (subunits) against the boiling point of the designated carbon fraction, the temperature at the 50% point as well as temperatures at 16 and 84% can be determined (Figure 11 and Table 2). A relatively complete description of the nature of the complex fuel mix will be available with three numbers. These express the 50% cutoff temperature and the temperature spread of the distillation cut of the majority of the components of the fuel.

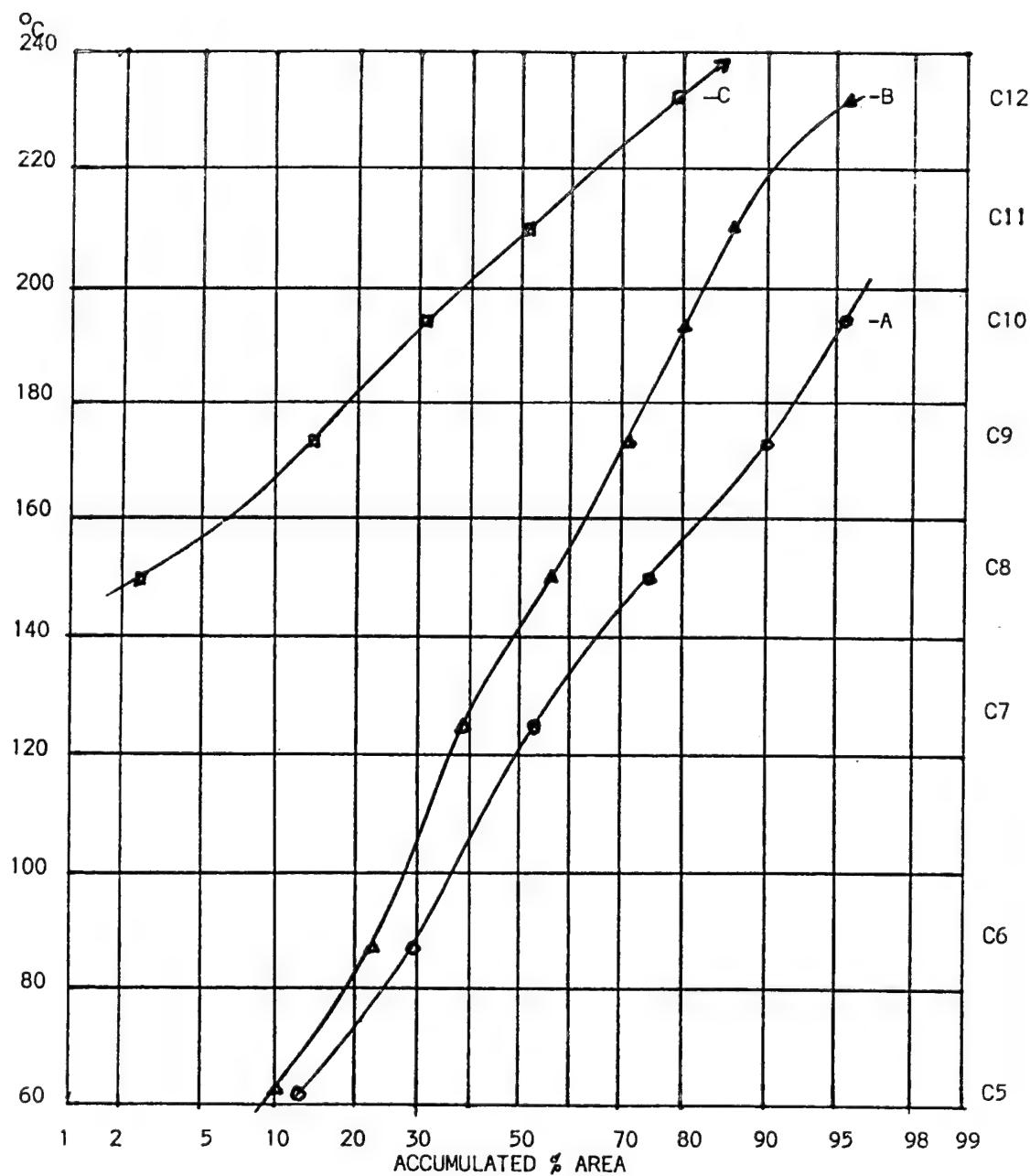


Figure 11. Probability plot of area slice data to determine the 16, 50, and 84% temperature cut-off points. A = Vapor, B = Liquid, C = Waste of Shale JP-4.

TABLE 2. SIMPLIFIED FUEL DESCRIPTION USING DATA OF ACCUMULATED PERCENT PEAK AREA FROM SIMULATED DISTILLATION OF SHALE JP-4

Phase	Accumulated %		
	16%	50%	84%
Liquid	73 °C	141 °C	205 °C
Vapor	66 °C	122 °C	161 °C
Waste	176 °C	209 °C	238 °C

Operational Problems

1. Temperature

The input air and fuel temperatures and that of the generation area itself were not completely controlled, having daily, as well as seasonal, and sometimes emergency fluctuations. These temperature fluctuations affected the tower efficiency, especially when the heat input was controlled with a specific rheostat setting and required adjustments to make up for changing conditions.

Variations in fuel viscosity due to temperature shifts affected the rotameter ball position for the same flow rate. Because a specific setting was predetermined for a study, corrections made to return the ball to that position slightly lowered flow when the fuel was colder and raised it when it was warmer.

During continuous studies, the operating parameters were checked at least hourly, and TPH concentrations were adjusted when outside a range of $\pm 5\%$ of targeted concentrations. Audible alarms were activated if the concentration exceeded $\pm 10\%$ of the desired concentration, and immediate attention was given to the problem. Minor adjustments were made using the chamber flow rate within limits rather than the generation system.

2. Splashing

The splashing of fuel at the bottom of the tower became a potential problem whenever the fuel input went above 13 mL/min. The droplets of the spent fuel hitting the hot glass wall in the zone of incoming air changed the composition of the vapor to include more of the heavier diesel range organics. When it occurred, this contributed to (a) the potential for aerosolization on cooling of the vapor, (b) to greater similarity of the chamber atmosphere with that of the supply material, and (c) to very rapid changes of chamber TPH concentration. A tower air input line modification extended the line above the pool of the spent fuel, thus reducing the probability of splashing from the bottom.

A similar result could have occurred if the inlet line separated from the glass wall and fuel falling through the air stream was blown against the hot glass or blown through as an aerosol. One report of the JP-8 study (Mattie et al., 1991) states that the entire fuel was vaporized. This idea may have resulted

from misidentification of samples, sampling problems, or the dropping through of liquid fuel. On searching archived records, it was observed that at times the record showed little difference between the atmosphere and the parent material as judged from the areas of a number of marker peaks. But with the inclusion of more of the available data and comparing a number of chamber vapor chromatograms, it appeared that at times fuel splashing or dropping through had occasionally occurred, but most of the time the vapor was composed as in the other studies favoring the more volatile components. As a method for getting a vapor more representative of the fuel itself, this phenomenon might deserve study.

3. Sampling

The Beckman 400 hydrocarbon analyzers were operated continuously. Samples were drawn from the chambers which operated at 20 mmHg negative to ambient, through 1/4 in. stainless steel lines, and pressurized by diaphragm pumps (Diapump, Model 08-800-70, Air Control Inc., Norristown, PA) to about 3 psi with flow about 3 to 4 L/min. Calibration was performed before each of the studies, and routine calibration checks were performed during the studies. The analyzers performed very well for extended periods without significant drifting of output signal. One early problem was a bleed-off of hydrocarbons from the pump check valves. This was corrected when each dome analytical system became independent and baseline air was delivered with a separate pump.

4. Chromatography

Headspace samples were used initially for determination of the benzene content. They were convenient and reasonably reproducible while serving the purpose intended. They also provided a method for quality control.

Dilution in hexane permitted an injection of a minute sample of the fuel presenting the first full chromatograms. But the presence of the hexane masked a problem encountered where approximately one-third of the barrels (the first five received) of shale JP-5 contained 3% aviation gasoline (AvGas), a contaminant from a tank at Rickenbacker Air Force Base (Figure 3). Even in the less contaminated samples from the rest of the supply, there was enough AvGas to cause a bimodal distribution in the vapor phase (Figure 3).

Delivering a valid vapor sample was a problem with the back pressures of the old packed column systems while the very low concentration studies created problems for the capillary systems. Generator output samples were sometimes invalid because of contamination with splashed or condensed fuels. Some apparent discrimination in TPH component distribution can be caused due to incomplete vaporization from the needle or the injection port. Generator output samples were potentially contaminated by recondensing vapors at the sample port. These required judgement when in disagreement with the chamber samples. Their advantage was that the concentration was much higher and the chromatograms more reliably integrated because they had flatter baselines.

Even though the chromatography data were from a variety of equipment, the data presented a consistent picture of all but the first few exposures. The JP-4 studies, shale and petroleum, differed somewhat from the rest with a significantly higher concentration of the front-end components, these being readily available in the parent mixture. The rest showed more similarity of the vapor phase to one another than would have been expected from differences in the liquid if not considering the limitations imposed by the component vapor pressures (Table 3).

The shale JP-5 contaminated with AvGas actually had a bimodal distribution of components in the vapor phase with all but complete stripping of the front-end materials from the fuel. The shale- derived JP-4 also appeared bimodal, but not as severely as the contaminated shale JP-5. There were some similarities in shale JP-4 front-end and petroleum JP-4. This could have been the result of a similar cracking process, contamination, or probably blending to achieve the required physical characteristics for a JP-4 type of the fuel containing significantly greater amounts of the lower fractions.

TABLE 3. AN ESTIMATION OF THE DISTRIBUTION OF THE MAJOR ALKANE FRACTIONS
PRESENT IN THE THREE PHASES OF THE FUELS

Fuel Type	Liquid	Vapor	Waste
P-JP-4	C7-C15	C6-C8	NA
S-JP-4	C5-C9-C13	C5-C9	C10-C14
P-JP-5	C10-C13	NA	NA
S-JP-5A	C6-C8-C13	C6-C7/C10-C11	C10-C13
S-JP-5	C10-C13	C10-C11	C10-C13
P-DFM	C11-C18	NA	NA
S-DFM	C11-C18	C8-C12	C11-C18
JP-7	C11-C14	C10-C12	NA
JP-TS	C9-C13	C9-C11	NA
JP-8	C9-C12	C9-C10	NA

Note: NA = not available

Operational Parameters

Tables 4, 5, and 6 contain some of the basic operational parameters gleaned from archival records of the studies reviewed. Many factors were involved in the choice of dome and generation flows. Some of these were (a) a benzene requirement, (b) limited fuel supply for the study, (c) minimal allowable dome flow, and (d) fielder's choice of the chemist within these restrictions.

TABLE 4. FUEL STUDY GENERATION CONDITIONS FOR PETROLEUM- AND SHALE-DERIVED JP-4

Study	JP-4 PET 348-351	JP-4 PET 510-512	JP-4 PET 540-542	JP-4 Shale 736-739	JP-4 Shale 756-759
Chemist	ERK	DIAZ	DIAZ	LEAHY	LEAHY
Date	Oct 73	Aug 79	Feb 80	Dec 83	Dec 83
Length	8 months	90 days	1 year	90 days	90 days
Type	6 h/day	24 h/day	6 h/day	24 h/day	24 h/day
Concentration (mg/L)					
High	5	1	5	1	1
Low	2.5	0.5	1	0.5	-
Dome Flows (CFM)	35-45	30-50	-	50-55	50-55
Fuel Flow (mL/min)	30-40	5.5 & 5.5	-	4.5 & 4.5	4.5
Evaporator (CFM)	2-3	4-5	-	4 & 4	4
Temperatures (°F)					
Top	-	-	-	86	86
Bottom	-	-	-	68	68

TABLE 5. FUEL STUDY GENERATION CONDITIONS FOR PETROLEUM- AND SHALE-DERIVED JP-5 AND DFM

Study	JP-5 PET 416-418	JP-5 S/A 490-492	JP-5 Shale 500-502	DFM-PET 436-438	DFM-Shale 530-532
Chemist	Leahy	Leahy	Leahy	Leahy	Leahy
Date	Jul 77	Apr 79	Jul 79	Nov 77	Dec 77
Length	90 days	60 days	90 days	90 days	90 days
Type	24 h/day	24 h/day	24 h/day	24 h/day	24 h/day
Concentration (mg/L)					
High	0.75	0.75	0.75	0.3	0.3
Low	0.15	0.15	0.15	0.05	0.05
Dome Flows (CFM)	30-40	30-50	30-50	40-50	30-50
Fuel Flow (mL/min)	10	10	10	13.5	8
Evaporator (CFM)	3.5	3	5.5	3.5	5
Temperatures (°F)					
Top	115-120	116	127	120	127
Bottom		91	91	90	115

TABLE 6. FUEL STUDY GENERATION CONDITIONS FOR JP-7, JP-TS, AND JP-8

Study	JP-7 PET 602-603	JP-TS PET 604-605	JP-8 PET 704-706
Chemist	DIAZ	DIAZ	DIAZ
Date	Apr 81	Apr 81	Apr 82
Length	1 year	1 year	90 days
Type	6 h/day	6 h/day	24 h/day
Concentration (mg/L)			
High	0.75	1.0	1.0
Low	0.15	0.2	0.5
Dome Flows (CFM)	30-40	30-40	28-38
Fuel Flow (mL/min)	16 & 16	15 & 15	15 & 15
Evaporator (CFM)	2.5 & 2.5	2.5 & 2.5	2.5 & 2.5
Temperatures (°F)			
Top	122	122	113
Bottom	-	86	86

SECTION 5
REFERENCES

Bishop, Edward C. 1981. Evaluating Health Hazards Associated With Aircraft Fuel Cell Maintenance. AFAMRL-TR-81-149, Proceedings of the Twelfth Conference on Environmental Toxicology, 3-5 November 1981.

Mattie, D.R., C.L. Alden, T.K. Newell, C.L. Gaworski, and C.D. Flemming. 1991. A 90-day continuous vapor inhalation toxicity study of JP-8 jet fuel followed by 20 or 21 months of recovery in Fischer 344 rats and C57BL/6 mice. *Toxicol. Pathol.* 19, 77.

Thomas, A.A. 1965. Low ambient pressure environments and toxicity. *Arch. Environ. Health* II, 316-322.